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PURIFICATION OF SMOKESTACK GASES OF AN ELECTRICAL GENERATING STATION OF SULFUR DIOXIDE USING THE MAGNESITE METHOD

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REPORT

PURIFICATION OF SMOKESTACK GASES OF AN ELECTRICAL GENERATING STATION OF SULFUR DIOXIDE USING THE MAGNESITE METHOD

[Ochistka dymouykh gazov elektrostantsiy ot sernistogo angidrida magnezitovym metodom]

No author given

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PURIFICATION OF SMOKESTACK GASES OF AN ELECTRICAL GENERATING STATION OF SULFUR DIOXIDE USING THE MAGNESITE METHOD

No author given

PROBLEM 8. A DESCRIPTION OF TEST METHODS, THE PLAN OF UPCOMING OPERATIONS AND THE METHOD OF ANALYTICAL CONTROL

Methods of Testing

Today work is continuing to improve the magnesite method of purification in laboratories of NIIOGAZ and on the experimental-operational installation of the Northern Donetsk thermoelectric generating station.

In the NIIOGAZ laboratories, typical installations are available for studying equilibrium in the gas-liquid system which are being used to verify existing data of the literature on the equilibrium of SO_2 vapor pressure over the absorbing suspensions used in the magnesite method.

In order to study equilibrium at low partial pressures of sulfur dioxide, a dynamic device is employed using the so-called "inert stream" method. The typical device and the method of operating it have been described in detail in the literature [for example, see V. A. Pinayev, Zhurnal prikladnoy khimii, (Journal of Applied Chemistry), 36, Number 10, 2116, (1963)].

In order to study the equilibrium and high partial pressures of sulfur dioxide (up to 76= mm Hg.), a static mercury vacuum device is employed in which the volume of absorbed sulfur dioxide is calculated according to the change in total pressure in the system. The typical device and the method of its operation have been described in the literature [see, for example, G. Ye. Braude, I. L. Leytes, I. V. Dedova, Khimicheskaya promyshlennost' (The Chemical Industry), Number 4, 232 (1961)].

In order to study the kinetics of oxidation of the sulfite-bisulfite solutions and to select inhibitors and catalysts of the oxidation process, dynamic devices are employed whose block diagrams are described in the literature [see, for example, A. V. Gladkiy, L. F. Sokolina, Yu. M. Afanas'yev, N. S. Torocheshnikov, Zhurnal prikladnoy khimii (Journal of Applied Chemistry, Vol. 46, Number 12, 2698 (1973)].

Apparatus with continuous bubbling or vessels with stirring devices are employed as reactors. The regime of the investigations is chosen such that the process occurs in the kinetic region, i.e., such that the rate of oxidation does not depend upon diffusion of the reacting components.

The investigation of the kinetics of recrystallization of magnesium sulfite crystals $MgSO_3 \cdot 6H_2O \longrightarrow MgSO_3 \cdot 3H_2O$ is also conducted in the thermostatic reactor with a mixer, from which samples are periodically taken for analysis. The methods of analytical control are described below.

Investigations on the absorption kinetics are conducted under laboratory conditions on typical devices described in the literature [see, for example, V. M. Ramm, Absorbtsiya gazov (Absorption of Gases), published by "khimiya", Moscow, (1966)]. Schematics of the test-operational devices have been described in previous reports.

Bubbling absorbers with various trays, an absorber with a nozzle-free direct Venturi tube, and film absorbers with ascending streams of gas and liquid have been used as absorption apparatus in the laboratory devices.

The apparatus used in the pilot and test-industrial devices have been described in previous reports.

During the study of absorption kinetics, the following were determined: the concentration of sulfur dioxide gases before and after purification; the concentrations of sulfite, sulfate and bisulfite in solutions before and after purification, the pH value of the absorbent; the S/L value in the absorbent, etc. Methods of analytical control are described below.

The effectiveness of purification is estimated via the degree of purification of the gas (α) and the general coefficient of mass transfer (Cmt).

$$\alpha = \frac{C_H - C_C}{C_H} \cdot 100\%$$

where C_H, C_C - concentration of SO_2 in the gas, respectively, before and after absorption.

$$C_{mt} = \frac{G}{\Delta p F(v)}, \quad \frac{kg}{m^2 hr. mm. Hg.} \quad \text{or} \quad \frac{kg}{m^3 hr. mm. Hg.}$$

where G - amount of SO_2 absorbed in the absorber, kg/hr;

Δp - motive force of the absorption process, mm. Hg.;

F(V) - surface (volume), on which contact of the gas and liquid occurs, m^2 (m^3).

$$\Delta p = \frac{(P_{int} - P^*_{out}) - (P_{out} - P^*_{int})}{2{,}3 \lg \frac{P_{int} - P^*_{out}}{P_{out} - P^*_{int}}}, \qquad (1)$$

where P_{int} - partial pressure of SO_2 in the gas, respectively, at the intake to the absorber and at its output, mm. Hg.

P^*_{int}, P^*_{out} - equilibrium pressure of SO_2 vapor over the absorbent, respectively at the intake to the absorber and at its output, mm. Hg.

The indicated method calculating Δp is just in a case when the line of equilibrium and the operating line are straight and the coefficient of mass transfer remains constant throughout the length of the apparatus. With a significant deviation of the equilibrium line from a straight line, the graphic method of calculating Δp is used.

Formula (1) is just in the presence of a counter stream of gas and liquid. When accomplishing purification in once-through apparatus, Δp is calculated as follows:

$$\Delta P = \frac{(P_{int} - P^*_{int}) - (P_{out} - P^*_{out})}{2{,}3 \lg \frac{P_{int} - P_{int^*}}{P_{out} - P^*_{out}}} \qquad (2)$$

In a case when $P^*_{int} = 0$ and $P^*_{out} = 0$, which frequently occurs in the magnesite method when conducting purification at high pH values of the absorbent (> 7,0), formulas (1) and (2) are simplified:

$$\Delta P = \frac{P_{int} - P_{out}}{2{,}3 \lg \frac{P_{int}}{P_{out}}} \qquad (3)$$

The Plan of Upcoming Operations

In the near future, the plan for improving the magnesite method contains provisions for conducting the following operations.

In the NIIOGAZ Laboratories, a.

1. Determining the expediency of employing the magnesite method at high SO_2 concentrations in the gases being purified (greater than 1%).

2. A study of the kinetics of recrystallization in the

$$MgSO_3 \cdot 6H_2O \rightarrow MgSO_3 \cdot 3H_2O$$

system, depending upon temperature and the content of magnesium sulfate in the solution.

3. Studying the kinetics of oxidation of magnesium sulfite-bisulfite solutions depending upon different parameters (concentration of sulfite and bisulfite ions, concentrations of magnesium sulfate, temperature). Establishing the mechanism of the oxidation process and the kinetic constants necessary for the technological calculations.

Seeking effective oxidation inhibitors with the goal of preventing or decreasing the formation of ammonium sulfate in the liquid phase, increasing the effectiveness of oxidation, and decreasing the content of magnesium sulfate and crystals of magnesium sulfate released from the system in drying and burning.

4. Determining the effectiveness of circulated magnesium oxide obtained after burning the crystals of magnesium sulfite (after several "absorption-regeneration" cycles).

This will be conducted under laboratory conditions due to the absence of a component for burning the magnesium sulfite crystals in the device at the Northern Donetsk installation.

5. A continuation of investigations to study the removal of magnesium trisulfite crystals from the system by the method of precipitation, with the use of effective flocculants. The study of the effect of different factors (concentrations of crystals, flocculants, and temperature).

6. A study of the rate of precipitation of inert impurities from the weakly acid solutions by the aid of effective flocculants, applicable to the preliminary extraction of impurities from the gases.

7. A study of reduction annealing of magnesium sulfite crystals, with the goal of obtaining elementary sulfur as a utilization product.

8. Conducting a comparative technical-economic calculation with the goal of choosing the most effective absorber from those studied earlier for practical application. To be conducted after the conclusion of the work in studying the kinetics of SO_2 absorption in different apparatus on the experimental-industrial installation of the Northern Donetsk thermoelectric generating station.

On the Pilot Installation of the Northern Donetsk Thermoelectric Generating Station

1. A determination of the effectiveness of inhibitor additives of oxidation during trials of the absorber with a movable spherical bed on the pilot installation.

Choosing the optimum concentration of the inhibitor and issuing recommendations for tests of the inhibitor under conditions of the experimental-industrial installation at the Northern Donetsk Thermoelectric Generating Station.

At the Experimental-Industrial Installation of the Northern Donetsk Thermoelectric Generating Station

1. A study of the low temperature magnesite method (obtaining magnesium hexasulfite crystals).

1.1. A study of SO_2 absorption kinetics in a two stage absorber with a Venturi tube. Within the following range of parameters: gas flow rate, 10-35,000 m^3/hr; flow rate of absorber suspension - 10-80 m^3/hr; pH value of absorber suspension $\sim$ 7.0; ratio of S/L in suspension $\sim$ 1/10; concentration of magnesium sulfate in absorbent $\sim$ 150-220 g/l; suspension temperature $\sim$ 45° C;

2. A study of the high temperature magnesite method (obtaining crystals of magnesium trisulfite).

2.1. A study of SO_2 absorption kinetics in the absorber with a movable spherical bed in the following range of parameters: gas velocity, 2-6 m/sec; density of irrigation - 15-100 m^3/m^2 hr; suspension temperature - 58-60° C; characteristics of the suspension are the same as during the study of the absorber with the Venturi tube. Static height of the spherical bed - 300-50 mm.

2.2. A study of hydrodynamics of an absorber with a movable spherical bed. Within the same range of hydrodynamic parameters.

2.3. Determining the effectiveness of additives of oxidation inhibitors during optimum hydrodynamic regimes (after obtaining recommendations on trials of the pilot device).

3. A continuation of investigations to study removal of magnesium trisulfite crystals from the system by the method of precipitation employing effective flocculants. The experiments are being conducted in a continuously operating sedimentation tank. The amount of suspension fed into the suspension tank is 0.5 - 5.0 m^3/hr. The program of tests will be updated following completion of the laboratory investigations.

4. A study of the yield of crystals by centrifuging, after preliminary thickening of the suspension by the precipitation method. After the conclusion of the indicated stage, an optimum method of removing the crystals or a combination of methods will be chosen.

5. A study of the removal of inert impurities for mildly acid solutions by the aid of precipitation (with the use of flocculants) and centrifuging. The program of tests will be updated after the completion of laboratory investigations. Following completion of the indicated stage, an optimum method of removing impurities or a combination of methods will be chosen.

6. A study of effective spray traps.

The program of tests is being carried out in the report according to the known method of oxygen potential, A-1 "Protokola".

METHODS OF ANALYTICAL AND PHYSICO-CHEMICAL CONTROL OF THE DEVICES FOR EXTRACTING SULFUR DIOXIDE USING THE MAGNESITE METHOD

1. Introduction

The basic parameters of the analytical physico-chemical control of the device for purification from SO_2 using the magnesite method are the following:

1. The concentration of SO_2 in the gas.
2. The ratio of the solid part of the suspension to its liquid phase. S:L (volume) of the working suspension.
3. S:L (gravimetric) of the working suspension.
4. Content of the solid phase in the suspension.
5. Acidity of the working suspension (pH) and of the solution.
6. Density of the working suspension and the solution.
7. Viscosity of the working suspension and the solution.
8. Moistness of the solid phase.
   ($MgSO_3$ crystals)
   a) (hygroscopic)
   b) (crystallizational)
9. Chemical composition of the liquid phase.
10. Chemical composition of the solid phase.
    ($MgSO_3$ crystals)
11. Chemical composition of the magnesite.

2. Analysis of the Gas

Determining SO_2 in the Gas.

The method is based on the oxidation reaction of sulfur dioxide and iodine:

$$SO_2 + I_2 + H_2O \rightarrow H_2SO_4 + 2HI$$

Reagents:

1) Iodine, 0.02 n solution
2) Sodium thiosulfate 0.02 n solution
3) Starch 0.5% solution

Course of the Analysis

The analyzed gas is pumped by a blower (or as the result of excess pressure in the system) through a gas pipette having a capacity of 1-1.5 l. for a period of 10 minutes at a rate ensuring no less than 10 times the volume of the pipette with respect to gas exchange.

After completing gas sampling, both valves of the pipette are simultaneously closed and the pipette is left in the laboratory for 10-15 minutes to equalize the temperature.

If the gas is sampled under pressure, after evening the temperature of the gas is brought to atmospheric pressure, releasing the excess gas by means of opening one of the pipette valves briefly.

If the gas is sampled by means of a blower under a vacuum, the value of rarefaction is measured with a manometer.

A funnel is connected to one of the valves and a certain amount of the iodine solution is poured into the funnel from a burette. The iodine is then poured into the pipette containing the gas sample. The iodine remnant is washed from the funnel with distilled water into the pipette.

The pipette is shaken for 2-3 minutes. Afterward, the solution from the pipette is poured into a 250 ml conical flask, into which the iodine is also poured from the walls of the pipette. Excess iodine in the flask is titrated with a 0.02 n solution of sodium thiosulfate with starch to the point of disappearance of the blue color (the indicator-starch is added at the end of titration).

With a SO_2 content in the gas of up to 0.3%, it is necessary to employ a 0.02 n solution of iodine and thiosulfate. When working with gases with high concentrations, one should use solutions of 0.05 n or 0.1 n. With a content of small amounts of SO_2 (hundredths or thousandths of a fraction of a percentage by volume) in the gases, which is usually characteristic for gases after absorption, analysis is conducted in the following fashion.

The analyzed gas is passed through a bubbler with a certain volume of solution. The volume of the passed gas is determined by gas hours or according to the volume of water flowing out of the aspirator.

The excess quantity of iodine is titrated out with a solution of $Na_2S_2O_3$.

The concentration of SO_2 in the gas is determined according to the following formula:

$$y = \frac{.032(N_I C_I V_I - N_T C_T V_T) P_{atm} (273 \cdot t)}{V(P_{atm} - R_{asp} - T_{H_2O}) 273} \quad g/l$$

where: 0.032 - amount of SO_2 corresponding to 1 ml 1 n solution I_2, g,

N_I, N_T - normality of iodine and thiosulfate.

C_I, C_T - correction coefficient for normality of iodine and thiosulfate,

V_I, V_T - volume taken for analyzing the solution of iodine and thiosulfate, ml,

P_{atm} - barometric pressure, mm Hg.,

t - temperature of gas taken for analysis, ° C,'

V - volume of gas taken for analysis, l,

R_{asp} - rarefaction in aspirator or gas pipette, mm Hg.

T_{H_2O} - tension of water vapor at the temperature of the experiment, mm Hg. (during use of the aqueous aspirator). The calculation can also be carried out according to the following formula:

$$y = \frac{(H_I c_I V_I - H_T c_T V_T) P_{atm} (273 + t) 21.9\ 100}{\text{[illegible]}\ 1200\ V (P_{atm} - R_{asp} - T_{H_2O}) 273} \quad \% \text{ Vol.}$$

3. Determination of S:L (of volume)

A sample of the suspension is taken from the moving stream or following intensive mixing.

10 ml suspension are poured from the sampler into a graduated cylinder and centrifuged for a period of 1-2 minutes. After centrifuging, the boundary of separation of the gases is determined and calculation is made of the relationship of the solid part of the suspension (S) to its liquid part (L). The numerator of (S) is arbitrarily expressed as 1.

Example: Sediment volume - 3 cm^3, solution volume - 7 cm^3
(S:L) volume = 3:7 = 1: 2.3.

4. Determining S:L (gravimetric)

The sample of the suspension is taken in a dry, previously weighed glass and is then filtered through a Buchner funnel into a dry Bunsen flask (the vacuum is created by means of a water stream pump, a blower, etc.).

The filtrate is transferred from the flask to the glass and weighed.

Calculation:

A - weight of empty glass, g,
B - weight of suspension with glass, g,
C - weight of filtrate with glass, g,

/C-A/ - weight of filtrate, g/L/

/B-c/ - weight of solid phase, g. /S/

$$S : L = \frac{B - C}{C - A} = I: \qquad \frac{C - A}{B - C},$$

5. Determining the Gravimetric Content of the Solid Phase in the Suspension

100 ml suspension are filtered under a vacuum through a previously dried and weighed paper filter on the Buchner funnel. The sediment from the filter is washed with an alcohol-acetone mixture. The filter with the sediment is placed in an hourglass on a dry shelf for 1 hour at 105° C, cooled in the exsiccator, and weighed.

Calculation: $S = (A-B) \cdot 10$ g/l

A - weight of sediment with filter, g.

B - weight of dried filter, g.

6. Determining Acidity (pH) of the Operating Suspension and the Solution

Mass produced pH-meters are employed for determining the pH value.

The relationship between values of pH and the content of magnesium sulfite and bisulfite in solution, characterized by the ratio of S/C (where S and C are the molar content of dissolved SO_2 and Mg), are expediently used to control the process of sulfur trapping in place of laborious chemical analyses.

This relationship is determined experimentally and is described by the following empirical equation (with S/C = 1.1 - 1.9)

$$lg\ pH - 0{,}83 - 0{,}9\ lg\ (\ S/C\ )$$

or

$$pH = \frac{6.76}{(S/C)^{0.9}}$$

7. Determining Density

The determination of the density of solutions and suspensions containing up to 100 g/l of the solid phase is made by the aid of hydrometers.

For suspensions containing more than 100 g/l solid phase, density is determined by the gravimetric method — by weighing a certain volume of the suspension.

Density "p" is expressed in g/cm^3 (kg/m^3).

8. Determining Viscosity

Dynamic viscosity is determined by the aid of the Hoppler viscosimeter whose operating principle is based upon measuring the duration of fall of a sphere of determined weight and size in a thermostatized cylinder.

Calculation of the values of dynamic viscosity is carried out according to the following formula:

$$\mu = \tau (\rho_1 - \rho_2) C$$, where

μ - dynamic viscosity, centipauses, CP.

τ - duration of fall of a sphere, sec.

P_1 - density of sphere, g/cm^3

P_2 - density of measured liquid, g/cm^3

C - permanent sphere, $\frac{cP \cdot cm^3}{g/sec}$
(given in the tables accompanying the instrument).

9. Analysis of the Solutions

A. Determining Magnesium Sulfite and Bisulfite with their Joint Presence in the Solutions

Separate determination of magnesium sulfite and bisulfite in solution is based on oxidation of HSO_3^- and SO_3^{2-} ions by iodine to SO_4^{2-} and on determining the amount of hydriodic and sulfuric acids formed in the oxidation process. Since sulfuric acid additionally forms in the process of oxidation of the bisulfite molecule, this makes it possible to determine the content of SO_3^{2-} and HSO_3^-, when both are present.

The reactions occur according to Equations 1, 2, 3 and 4.

$$Mg(HSO_3)_2 + 2I_2 + 2H_2O \rightarrow MgSO_4 + 4HI + H_2SO_4 \quad (1)$$

$$4HI + H_2SO_4 + 6KOH \rightarrow 4KI + K_2SO_4 + 6H_2O \quad (2)$$

Oxidation of magnesium sulfite occurs according to the following reactions:

$$MgSO_3 + I_2 + H_2O \rightarrow MgSO_4 + 2HI \quad (3)$$

$$2HI + 2KOH \rightarrow 2KI + 2H_2O \quad (4)$$

Symbols:

X = number of moles of $Mg(HSO_3)_2$

Y = number of moles of $MgSO_3$

According to Equations (1) and (2):

1 mole $Mg(HSO_3)_2$ = 2 moles I_2 = 6 moles KOH

According to Equations (3) and (4): 1 mole $MgSO_3$ = 1 mole I_2 = 2 moles KOH.

The number of moles of iodine consumed for the oxidation of $Mg(HSO_3)_2$ and $MgSO_3$ is:

$$I_2 = 2x + Y \tag{5}$$

$$\text{The number of moles of KOH} = 6x + 2Y \tag{6}$$

In solving Equations (5) and (6) together, one can write:

$$2x = KOH - 2\ I_2, \text{ i.e.,}$$

$$x = \frac{KOH - 2\ I_2}{2}$$

Shifting to equivalents, we obtain:

$$\frac{2x}{4} = \frac{KOH}{I} - \frac{2\ I_2}{2} \quad \text{or} \quad 2x - 4\ KOH - 4\ I_2 \text{ and}$$

$$x = /KOH - I_2/\ 2$$

Thence

$$g/l\ Mg(HSO_3)_2 = 0.00465 \cdot 1{,}000/KOH - I_2/ \cdot 2$$

Similarly: $KOH - 6x + 2y$

$$\frac{3\ I_2 = 6x + 3y}{3\ I_2 = KOH = y} \quad \text{of}$$

Shifting to the equivalents: $\frac{3\ I_2}{2} = \frac{KOH}{1} = \frac{I}{2}$ and

$$y = (1.5\ I_2 - KOH)\ 2$$

Thence,

g/l $MgSO_3$ = 0,0052 · 1000/1,5 I_2 - KOH / · 2

Reagents:

1) Iodine, 0.1 n solution
2) sodium thiosulfate, 0.1 n solution
3) caustic soda, 0.1 n solution (or KOH)
4) starch, 0.5% solution
5) mixed indicator

Course of the Analysis

10 ml solution of magnesium sulfite-bisulfite-sulfate is drawn into a pipette from the sample of the working suspension via a glass nozzle with a paper filter. The suspension is placed in a 100 ml measuring flask into which 50 ml distilled water has been previously poured. A volume of liquid is added to the flask to the mark and is carefully stirred. 10 ml solution is taken from the measuring flask with a pipette, and is placed in a conical 250 ml flask while stirring, to which 25 ml 0.1 n iodine solution has been previously added. The contents of the flask are stirred once again and excess iodine is titrated with a 0.1 n solution thiosulfate in the presence of the indicator — starch — to the point of disappearance of the blue color.

Two - three drops of mixed indicator are added to the solution titrated with thiosulfate and the liberated acid is titrated with an alkali solution to the point of a change in color from violet to green.

Note: For rapid analysis of the operating solution, one can take 1 ml undiluted filtered solution.

$$Mg(HSO_3)_2 = 93\ (V_1N_1C_1 - V_2N_2C_2) \quad g/l$$

$$Mg(SO_3) = 104\ (1.5\ V_2N_2C_2 - V_1N_1C_1) \quad g/l$$

where V_1 - amount ml solution KOH of that expended on titration

V_2 - amount ml solution I_2 bound in the course of analysis

N_1 - normality of KOH solution

N_2 - normality of I_2 solution

C_1 - correction coefficient of the KOH solution

C_2 - correction coefficient of the I_2 solution

B. Determining Total Magnesium and Calcium in Solution

Complexometric determination of magnesium is based upon the property of trilon B, which is a disodium salt of ethylendiaminotetracetic acid, to form stable complex compounds with the ions of bivalent metals, specifically, with the ions of magnesium and calcium.

If an indicator — YeT-00 chromogen black is introduced into a solution containing ions of magnesium or calcium — the indicator yields colored compounds with these ions — then upon adding trilon B to such a stained solution, a change in color will occur at the equivalent point, corresponding to binding of all ions of magnesium/calcium/in complex by the trilon B.

Note: In case Fe^{3+} or Al^{3+} ions are present, interfering with determination, the latter are bound in complexes by adding 5 ml 1% solution triethanolamine:

Reagents:

1) trilon solution - 0.1 n.
2) ammonium-ammonia buffer solution
3) YeT-00 chromogen black indicator
4) $MgSO_4$ solution, 0.1 n (fixanal - fiksanal)
5) HCl solution/1:1/.
6) murexide (mureksid) indicator (powder)
7) solution NaOH 20%

The Analysis

In the absence of calcium ions in the solution, titration of magnesium with trilon B is conducted with the YeT-00 chromogen-black indicator. The content of calcium, in the case of its presence, is determined in a separate test with the murexide (mureksid) indicator.

a. In order to determine Mg^{2+} or total Mg^{2+} and Ca^{2+}, 10 ml filtered working solution are transferred to a 100 ml measuring flask, brought up to the mark with distilled water, and carefully stirred. 5 ml of the obtained solution are drawn off, placed in a 250 ml conical flask, 10 ml ammonium-ammonia buffer solution and 7-8 drops chromogen black YeT-00 indicator are added, after which the solution is slowly titrated with 0.1 n trilon B solution with intensive stirring until the color of the solution changes from raspberry-red to blue.

Calculation:

$$Mg^{2+}_{tot} = \frac{a \cdot H \cdot C \cdot 24,32 \cdot 100 \cdot 1000}{2 \cdot 1000 \cdot 5 \cdot 10} \quad g/l$$

or $$Mg^{2+}_{tot} = a \cdot C \cdot 2,432 \quad g/l, \text{ where}$$

a- expenditure of trilon B, 0.1 n, ml

C- correction coefficient of trilon B.

$\frac{24.32}{2}$ - gram equivalent of magnesium with respect to trilon B.

b. In order to determine Ca^{2+}, 5 ml solution are drawn from the measuring flask with a pipette and placed in a 250 ml conical flask 20% NaOH is added drop-by-drop until pH=12 is reached (pH is determined by indicator paper or potentiometrically), and then a small excess amount of NaOH is added — 2-5 drops, followed by 3-4 crystals of muroxide indicator, and, during intensive stirring, the solution is slowly titrated with a solution of trilon B until the color of the solution changes from rose to violet.

Calculation:

$$Ca^{2+} = \frac{\cdot H \cdot C \cdot 40.08 \cdot 1000 \cdot 100}{2 \cdot 1000 \cdot 5 \quad 10}$$

or Ca^{2+} = b · C · 4,008 g/l, where

b = expenditure of trilon B, 0.1 n., ml

C = correction coefficient of trilon B,

$\frac{40.08}{2}$ = gram equivalent of calcium for trilon B

With the combined presence of Mg^{2+} and Ca^{2+} in the solution, calculation is made according to the following formula

$$Mg^{2+}_{tot} = (a - B)\ C \cdot 2,432$$

C. Determining Magnesium Thiosulfate in the Sulfite-Bisulfite Solution by the Formaldehyde Method

During the reaction with formaldehyde, magnesium sulfite and bisulfite enter into compounds that do not react with iodine.

After acidification of the solution with acetic acid, magnesium thiosulfate is titrated with iodine.

Reagents:

1) iodine, 0.1 n solution
2) formalin, 40% solution
3) acetic acid, 10% solution
4) starch, 0.5% solution

Course of the Analysis

25 ml filtered solutions are placed in a 250 ml conical flask. 5 ml 40% formalin are added to the flask. 5 minutes later, 15 ml 10% CH_3COOH are added and the solution is titrated with a 0.1 n iodine solution in the presence of starch until the appearance of a blue color.

Calculation: $MgS_2O_3 = aC \frac{13.6}{25}$ g/l, where

a - amount of ml iodine, 0.1 n., expended on titration;

C - correction coefficient of 0.1 n iodine;

13.6 - gram equivalent of 0.1 n solution MgS_2O_3

D. Approximate Calculation of $MgSO_4$ in Solution

The derivative solutions of the sulfur trap contain the following magnesium salts: sulfate, sulfite, bisulfite, and the thiosulfate of magnesium.

In the presence of analyses for magnesium sulfite and bisulfite, the content of $MgSO_4$ can be calculated, having determined total magnesium in the solution trilonometrically.

Calculation formula:

$$Mg\ SO_4 = [\ Mg^{2+}_{tot} - (0.129\ Mg(HSO_3)_2 + 0.231\ Mg\ SO_3)]\ 5,\ g/l,\ \text{where}$$

$0.129 = \frac{24}{186}$ - conversion factor of bisulfite for magnesium

$0.231 = \frac{24}{104}$ - conversion factor of sulfite for magnesium

$5 = \frac{120}{24}$ - conversion factor of magnesium for magnesium sulfate

E. Determining Magnesium Sulfate in Solution by the Gravimetric Method

Magnesium sulfate is determined by the precipitation method using barium chloride according to the reaction

$$SO_4^{2-} + Ba^{2+} \rightarrow BaSO_4$$

Precipitation of barium sulfate is carried out in an acid medium at a temperature near the boiling point.

Reagents:

1) barium chloride, 5% solution
2) diluted hydrochloric acid (1:1)
3) 0.1% solution methyl orange
4) silver nitrate, 1% solution.

Course of the Analysis

25 ml filtered sulfite-bisulfite-sulfate solution are placed in a 250 ml measuring flask, brought up to the mark with distilled water, and stirred. 10 ml diluted solution are taken for analysis with a pipette and placed in a 400-500 mm chemical glass, diluted with water to ~ 200 ml and acidified with HCl (1:1) according to methyl orange. Then the solution is heated almost to the boiling point and 20 ml 5% solution $BaCl_2$ are slowly added.

When adding the $BaCl_2$, the solution is constantly stirred. The completeness of precipitation of SO_4^{2-} is checked when adding several drops of $BaCl_2$ to the transparent clarified solution. After complete precipitation of $BaSO_4$, the flask is covered with a glass and is placed in a sand bath for 1-2 hours (=70 - 80° C) or is left to stand without heating for 12-16 hours. Filtration is carried out through a dense non-ash filter (blue tape), pouring the liquid from the sediment onto the filter first.

In order to remove particles of the sediment adhering to the sides of the flask, a glass rod with a rubber tip is used. The sediment must be completely applied to the filter, where it is washed with hot water to remove the Cl^- ions (test for $AgNO_3$). After washing, the filter and the sediment are carefully placed in a porcelain crucible that has been previously calcined, cooled in an exsiccator and weighed. The filter is dried, burned, and the residue is sintered at a temperature of t = 800 - 900° C for a period of 20-30 minutes, cooled in an exsiccator for 30-45 minutes and weighed.

Calculation is carried out according to the following formula:

$$MgSO_4 = \frac{0.516 \cdot a \cdot 1000 \cdot 250}{25 \cdot 10} \quad g/l, \text{ where}$$

a - weight of sediment, g

$\frac{250}{25 \cdot 10}$ - dilution $0.516 - \frac{MgSO_4}{BaSO_4} = \frac{120.37}{233.4}$ Conversion factor

10. Analysis of the Solid Phase (Crystals)

A. Determining the Chemical Composition of the Solid Phase

Samples of the suspension are taken from the moving stream or following intensive mixing.

The solid phase is separated from 100 ml suspension in a Buchner funnel and is washed with an alcohol-acetone mixture (1:1).

In order to determine moistness, 1 g is taken and the remainder of the solid phase (the crystals are placed in a drying cabinet for 3 hours at a temperature of 180° C.) From this dried sample, suspensions are taken for determining $MgSO_3$, MgO, Mg^{2+}_{tot}, $MgSO_4$, and other components.

B. Determining the Moistness of the Crystals

The total amount of hygroscopic and crystallization moisture comprises the total moistness of magnesium sulfite crystals. Depending upon the purpose of the analysis, one can determine total moisture or crystallization and hygroscopic moisture separately.

C. Hygroscopic Moistness

About 1 g weighed quantity of crystals, taken on the analytic scales, is placed in a preliminarily weighed box (the latter should be well dried and stored in a closed exsiccator with calcium chloride). The open box with the weighed quantity of crystals is placed in an exsiccator with concentrated sulfuric acid poured into it, specific gravity 1.84. The weighed quantity is dried over H_2SO_4 for 2-3 days and upon reaching a constant weight, calculation is made:

$$\% \text{ hygroscopic moistness} = \frac{B-C}{B-A} \cdot 100, \text{ where}$$

A - weight of empty box,

B - weight of box with weighed quantity,

C - weight of box with weighed quantity after drying in the exsiccator.

D. Crystallization Moistness

After determining hygroscopic moistness, the weighed quantity is placed in a drying cabinet and at a temperature of 180° is dried to a constant weight over the course of about 3 hours. The box is cooled in an exsiccator containing $CaCl_2$ and is weighed. Calculation is carried out according to the following formula:

$$\% \text{ crystallization moistness} = \frac{(C-D) \cdot 100}{C-A}, \text{ where}$$

D - weight of box with weighed quantity after drying in the drying cabinet (g).

Determination of crystallization moisture in the mixture of hexa- and magnesium sulfite trihydrate.

Calculation is made per molecule of magnesium sulfite.

A - weight of empty box, g.

B - weight of box with weighed quantity,

C - weight of box with weighed quantity after drying at 60° C,

D - weight of box with weighed quantity after drying at 180° C

C-A - weighed quantity for calculating crystallization moisture

C-D - crystallization moisture,

(C-A) - (C-D) $MgSO_3$, g

$\frac{C-D}{18}$ moles H_2O (X)

$\frac{(C-A) - (C-B)}{\ldots 104}$ moles $MgSO_3$ (Y)

$\frac{X \cdot X}{Y}$ moles H_2O per molecule $MgSO_3$

E. Total Moistness

The weighed quantity of sulfur crystals (∿ 1 g) is placed in the weighed box and dried in a drying cabinet at t = 180° C for 3 hours.

After cooling in the exsiccator and weighing, the calculation is made; % total moisture = $\frac{B-D}{B-A} \cdot 100$

(for symbols, see above)

F. Determining the Residue Insoluble in Acid

A weighed quantity of 0.5 g taken from the crystals dried at 180° C is placed in a chemical beaker and 30 ml HCl (1:1) are poured in. The mixture is brought to solution at a temperature of ∿ 80° C over the course of

20-25 minutes. After dissolving the weighed quantity, 30-40 ml distilled water is added to the beaker and the solution is filtered through a paper filter that has been preliminarily dried at a temperature of 105° C and weighed. The filtrate is used for subsequent measurements.

The sediment on the filter is washed with hot distilled water to remove Cl^- ions, after which it and the filter are placed in a drying cabinet and dried to a constant weight at a temperature of 100 - 105° C. After cooling and weighing the residue with the filter, calculation of the insoluble residue is made (I/R):

$$\% \text{ I/R} \quad X = \frac{A - B}{g} \cdot 100, \text{ where}$$

A - weight of dried filter with insoluble residue,
B - weight of dried filter,
g - weight quantity of crystals, g.

The weighed I/R and the filter are placed in a porcelain crucible (preliminarily calcined and weighed). The filter and the H/O are burned and sintered in a muffle furnace at a temperature of 800 - 900° C to a constant weight. The crucible is cooled in an exsiccator for 30-45 minutes and weighed. The insoluble residue after sintering is determined in this way.

$$\% \text{ I/R (after sintering)} = \frac{C}{g} \cdot 100, \text{ where:}$$

C - weight of residue, g,
g - weighed quantity (g).

G. Determination of the Sesquioxides

Reagents:

1) hydrogen peroxide, 3% solution
2) ammonium chloride, 2% solution

3) - ammonia, 12% solution

4) - silver nitrate, 1% solution

Course of the Analysis

10 ml 3% H_2O_2 are added to the filtrate after determining the residue insoluble in acid in order to oxidize Fe^{2+} to Fe^{3+}. The solution is boiled for 15 minutes to remove the excess oxidant. Then 30-40 ml 2% NH_4Cl are added to create an ammonia-alkali medium, the solution is cooled to 70-80° C, and 12% NH_4OH are separated out to the appearance of flakes and the odor of ammonia. The residue is filtered through a filter with a white tape into a 500 ml measuring flask (for subsequent measurements of SO_4^{2-}, Ca^{2+}, Mg^{2+}, etc.) and is washed to remove Cl^- (test with $AgNO_3$). The filter containing the sediment is transferred to a sintered and weighed crucible, dried, burned, and sintered at a temperature of 800° C. Then it is cooled in an exsiccator for 30-45 minutes and weighed.

Calculation:

$$\% \; R_2O_3 = \frac{a \cdot 100}{g}$$

a - weight of sediment, g.

g - measured quantity, g.

H. Determining Magnesium Sulfate in Crystals by the Gravimetric Method

Magnesium sulfate is determined in the form of barium sulfate.

Reagents:

1. barium chloride, 5% solution.
2. hydrochloric acid, diluted (1:1)
3. methyl orange, 0.1% solution
4. silver nitrate, 1% solution

Course of the Analysis

After separating the sesquioxides from the measuring flask, 100 ml filtrate are taken by means of a pipette and placed in a 500 ml flask where it is acidified with hydrochloric acid (1:1) according to methyl orange until the color changes from yellow to rose. It is then heated almost to the boiling point and 30-40 ml 5% barium chloride is slowly poured in. The solution is constantly stirred when adding the $BaCl_2$. The sediment is collected on the bottom of the flask over a period of 20-30 minutes and the completeness of precipitation is checked, adding several drops of the barium chloride solution to the transparent liquid over the precipitate. If a precipitate forms during this process, another 10 ml $BaCl_2$ solution is added and the precipitate is once again permitted to settle on the bottom and the completeness of precipitation is checked again.

After complete precipitation, the flask is covered with an hourglass and placed for 1-2 hours in a sand bath (t = 70-80° C). If possible, the solution is allowed to stand over night.

The solution is filtered through a dense non-ash filter (blue tape), first pouring the transparent liquid from the sediment onto the filter. The first portions of the filtrate are checked for the completion of precipitation of SO_4^{2-}, adding a few drops of $BaCl_2$ to it.

In order to remove the sediment particles adhering to the sides of the glass, a glass rod with a rubber tip is used.

The sediment must be totally transferred to the filter, which is washed with hot water to remove Cl^- ions (test for $AgNO_3$).

After washing, the filter and the sediment are carefully transferred to a ceramic crucible that has been previously sintered, cooled in an exisiccator and weighed. The filters are dried and burned and the sediment is sintered at a temperature of 800 - 900° C for a period of 20-30 minutes,

cooled in an exsiccator for 30-45 minutes and weighed.

Calculation is made according to the following formula:

$$\% MgSO_4 = \frac{0,516 \cdot a}{g} \cdot 100,$$ where:

a - weight of sediment, g

g - weight of measured quantity, g.

$$0,516 = \frac{M\ MgSO_4}{M\ BaSO_4} = \frac{120,37}{233,4}$$ - conversion factor

I. Determining $MgSO_3$, MgO and Mg_{tot} in Crystals

(from a single weighed quantity)

Magnesium sulfite is oxidized with an iodine solution to magnesium sulfate according to the following reaction:

$$MgSO_3 + I_2 + H_2O \rightarrow MgSO_4 + 2HI$$

In view of the poor solubility of magnesium sulfite, this reaction basically proceeds on its surface. In order to accelerate the reaction, HCl is added:

$$MgSO_3 + 2HCl \rightarrow MgCl_2 + SO_2\uparrow + H_2O$$

The liberated SO_2 immediately enters into reaction with the iodine and is oxidized: $$SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI$$

MgO, present in the crystals, reacts with HCl

$$MgO + 2HCl \rightarrow MgCl_2 + H_2O$$

Reagents:

1. iodine, 0.1 solution
2. hydrochloric acid, 1 n solution
3. caustic soda, 1 n solution
4. trilon B, 0.1 n solution
5. starch, 0.5% solution
6. mixed indicator
7. YeT-00 chromogen black

Course of the Analysis

The measured quantity of crystals dried at 180° C, equal to 0.1 - 0.2 g, is placed in a 250 ml conical flask to which 25 ml 0.1 n I_2 and 25 ml 0.1 n HCl have been previously added.

The contents of the flask are stirred until complete solution of the crystals (only the residue insoluble in the acid may remain in the bottom of the flask).

Excess iodine is titrated off with a 0.1 n solution thiosulfate (starch is added before terminating titration).

In order to determine MgO in the thiosulfate titrated sample, 2-3 drops of mixed indicator are added. Excess acid is titrated off with a 0.1 n NaOH solution until the color changes from violet to green.

After determining $MgSO_3$ and MgO in the solution, Mg^{2+}_{tot} is determined trilonometrically. 10 ml ammonium-ammonia buffer solution and 7-8 drops of freshly prepared YeT-00 chromogen black indicator are added to the solution in the flask, after which the solution is slowly titrated with a 0.1 n solution of trilon B while intensively stirring until the color of the solution changes from a raspberry-red color to blue.

Calculation:

$$\% MgSO_3 = \frac{(a-a_1)\,C\,N\;104.32}{g \cdot 2 \cdot 1000} \cdot 100$$ or

$$\% MgSO_3 = \frac{(a-a_1)\,C\;0.5216}{g}$$

$$\% MgO = \frac{[b\,C\,N_1 + (a-a_1)\,C\,N - (S\,C_1\,N_1)]\,40.32 \cdot 100}{g \cdot 2 \cdot 1000}$$ or

$$\% MgO = \frac{[(a-a_1)\,C\,N - (S-b)\,C_1\,N_1]\,2.016}{g}$$

$$\% Mg^{2+}_{tot} = \frac{d \cdot C_2\,N_2 \cdot 24.32\;100}{g \cdot 2 \cdot 1000}$$

or

$$\% Mg^{2+}_{tot} = \frac{d \cdot C_2 \cdot 0.1216}{g}$$

where

a - amount in ml of 0.1 n $Na_2S_2O_3$ necessary for reaction with 25 ml 0.1 n I_2 (blank test)

a_1 - amount in ml 0.1 n $Na_2S_2O_3$ going for inverse titration of the non-reacted iodine.

N - normality of $Na_2S_2O_3$

C - coefficient of 0.1 n $Na_2S_2O_3$

g - measured quantity, g.

b - amount in ml, 0.1 n NaOH necessary to titrate 25 ml 0.1 n HCl taken for solution

S - amount in ml 0.1 n NaOH spent on titration of excess acid.

N_1 - normality of alkali

C_1 - coefficient of 0.1 n NaOH

d - amount in ml of 0.1 n trilon B spent on titrating Mg^{2+}_{tot}.

N_2 - normality of trilon B

C_2 - coefficient of trilon B

J. Photometric Determination of Iron with Sulfosalicyclic Acid

Sulfosalicylic acid forms a yellow compound in an ammonium solution with both the ions of Fe^{2+} and ions Fe^{3+}. This is one of the significant advantages of this method. When determining the total content of iron, neither preliminary oxidation nor preliminary reduction are required, and at the same time (see below) it is possible separately to determine both forms of iron.

The intensity of the obtained stain does not practically depend upon the amount of ammonia added. In acid solutions, the same reagent forms a red compound only with Fe^{3+}.

The intensity of the stain depends upon the concentration of the acid and therefore it is unnecessary to add a buffer solution. With a change in the pH value, the maximum of light absorption shifts. The molar coefficient of absorption is $\varepsilon = 600$ with $\lambda = 430$ millimicrons. With pH = 1.5, the maximum is found at a value of $\lambda = 500$ millimicrons; pH = 5.0, $\lambda = 460$ millimicrons.

Phosphorous does not interfere with the determination of iron.

With Ca^{2+} and Mg^{2+} present in the solution, ammonium orthophosphate is added and the strong oxidants should be absent. In both the acid and the alkali medium, one can determine from 0.25 to 8.0 mg/l iron.

Most often, the total content of iron in the alkali medium is determined. Since Al^{3+} and Mg^{2+} form compounds with sulfosalicylic acid, when preparing the standard solution for plotting the calibration curve, magnesium sulfite and

aluminum sulfite are added to the Mohr salt.

Reagents:

1. sulfosalicylic acid, 10% solution or sodium sulfosalicylate, saturated solution.
2. diluted ammonia solution (2:3)
3. hydrochloric acid (1:1)
4. ammonium or potassium per sulfate ($C_2S_2O_8$)
5. Mohr's salt, $FeSO_4\ (NH_4)_2SO_4.6H_2O$ (recrystallized)
6. Aluminum sulfate
7. Magnesium sulfate

Preparation of the standard solution containing 0.2 g/l Fe^{3+}, 0.2 g/l Al^{3+} and 6.0 g/l Mg^{2+}.

0.140 g Mohr's salt are taken for preparing 100 ml standard solution - $FeSO_4\ (NH_4)_2SO_4 \cdot 6H_2O$, 0.127 g. aluminum sulfate - $Al_2\ (SO_4)_3$ and 5.950 g magnesium sulfate - $MgSO_4 \cdot 7H_2O$ are dissolved in a measuring flask.

A standard scale is compiled for plotting the relationship of optical density "D" and the concentration of Fe^{3+} from the obtained solution by appropriate dilution and a calibration curve is constructed. For this purpose, the prepared solutions are successively poured into a selected cuvette (cuvette = 5.095 mm) of the photocolorimeter FEKN and calculation of the optical density is made by employing the number 2 blue light filter at a wavelength λ = 413 millimicrons. The investigated working solutions are then poured into the same cuvette. One finds the concentration of Fe^{3+} in the working solution in g/l according to the value of "D" and the calibration curve.

Determination of Fe^{3+} in the crystals is carried out similarly to the solution.

Course of the Determination

25 ml filtered solution, 1 ml HCl (1:1), approximately 0.2 - 0.5 g ammonium or potassium per sulfate are added to a 100 ml measuring flask. The sample is boiled for 7-10 minutes, then cooled, and 10 ml 10% solution sulfosalicylic acid are added. The sulfosalicylic acid with Fe^{3+} yields a yellow complex at a pH of 8.5 - 11.0. The necessary pH is created by adding ammonia, then the sample volume is brought to the mark with distilled water. The solution is stirred and poured into a cuvette for colorimetry.

Iron content in the solution is calculated according to the following formula: C = 0.09D, g/l

where C - content of iron in solution, g/l

D - optical density of the solution.

11. Analysis of the Magnesite

A. Determining Moistness of the Magnesite

The weighed quantity of magnesite ground in the mortar ∿1 g is placed (in a previously dried and weighed) weighing bottle and is dried in a drying cabinet for 3 hours at t = 200° C.

Calculation: $\%\ \text{mois.} = \frac{B - C}{B - A} \cdot 100$, where

A - weight of empty weighing bottle, g.

B - weight of weighing bottle with weighed quantity, g.

C - weight of weighing bottle with weighed quantity, after drying, g.

B. Determining Loss During Calcination (calcination loss)

A weighed quantity of 1 g, taken from the ground magnesite powder, is placed in a porcelain crucible (calcined) and is calcined in a muffle

furnace at t = 1050 - 1100° C for 1 - 1.5 hours.

The crucible is weighed after cooling in an exsiccator.

Weight loss corresponds to calcination losses.

% Calcination loss = $\frac{A - B}{g}$. 100, where

A - weight of crucible with weighed quantity before calcination, g

B - weight of crucible with calcined weighed quantity, g.

g - weighed quantity of magnesite, g.

C. Determining the Residue Insoluble in Acid

A weighed quantity of 0.5 g ground commercial magnesite is dissolved in a porcelain beaker in 30 ml HCl, and is evaporated dry in a sand bath. Then 20-30 ml HCl are once again added (1:1), diluted with distilled water, and the contents of the beaker are filtered into a 250 ml measuring flask for subsequent determination of Mg^{2+}_{tot}. The sediment in the filter is washed several times with hot distilled water, after which the filter and the sediment are transferred to a weighed, calcined crucible, dried, and placed in a muffle furnace, where the sediment is calcined to a constant weight at t = 950 - 1000° C.

Calculation:

$$\% \text{ n/o} = \frac{A - B}{g} \cdot 100, \quad \text{where}$$

A - weight of crucible with calcined sediment, g.

B - weight of dry crucible, g.

g - weighed quantity, g.

D. Determining Mg in the Magnesite

Mg^{2+}_{tot} in the magnesite is found trilonometrically and then conversion is made for MgO.

Reagents:

1. trilon B, 0.1 n solution.
2. ammonia buffer solution
3. ammonium-ammonia buffer solution
4. YeT-00 chromogen-black indicator
5. hydrochloric acid, diluted (1:1)
6. mixed indicator
7. ammonia, 25% solution

Course of the Analysis:

The filtrate (after separating H/O) is placed in a 250 ml measuring flask, brought up to the mark, and carefully stirred.

25 ml solution is taken for analysis with a pipette and is placed in a conical flask. 15-20 ml ammonia-buffer solution, and 7-8 drops of YeT-00 chromogen black indicator are placed in the flask, bringing the volume of the solution to 75-100 ml with distilled water. The solution is then slowly titrated with a 0.1 n trilon B solution during intensive stirring until the color changes from raspberry-red to blue.

Calculation:

$$\%\ MgO = \frac{C \cdot 0,001216 \cdot 250 \cdot 40,32}{g \cdot 25 \quad 24,32} \cdot 100, \text{ or}$$

$$\%\ MgO = \frac{\ell\ C}{g} \cdot 2,032 \quad \text{where}$$

ℓ - amount of trilon B, ml

C - correction coefficient of trilon B

$\frac{250}{25}$ - dilution

g - weighed quantity of sample, g.

1 ml 0.1 n trilon B solution corresponds to 0.001216 g Mg.

E. Determining the Activity of the Magnesite (arbitrary activity)

0.3 g well ground magnesite is placed in a 250 ml flask and exactly 50 ml 1 n HCl are added.

The contents of the flask are heated for 2-5 minutes and the solution is continuously stirred.

Excess acid is titrated off with a 1 n solution of NaOH in the presence of mixed indicator until the color changes from violet to green.

Calculation:

$$\% MgO = \frac{(a - B) \cdot N \cdot 40{,}32 \cdot 100 \cdot C}{g \cdot 2 \cdot 1000}$$,where

a - ml. 1 n alkali required to titrate acid taken for solution;

B - ml. 1 n alkali spent on inverse titration;

N - normality of alkali

C - correction coefficient of the 1 n solution

$\frac{40 \cdot 32}{2}$ - gram equivalent of MgO.

F. Determining MgO in the Magnesite Milk Prepared in Water (concentration greater than 1%).

The determination of MgO is made by means of trilonometric analysis for total magnesium, with subsequent conversion of the results for MgO. In this case, the CaO contained in the milk is disregarded in view of its insignificant quantity.

Reagents:

1. trilen B, 0.1 n solution
2. ammonia buffer solution,
3. ammonium-ammonia buffer solution
4. YeT-00 chromogen-black indicator
5. hydrochloric acid, 1:1
6. mixed indicator
7. 25% ammonia solution

Course of the Analysis

10 ml magnesite milk (sampling is carried out by means of a pipette or a calibrated test tube), are removed to a conical 250 ml flask and 50 ml HCl (1:1) are added. The solution is heated for 20-30 minutes at a temperature of 60-70° C. After dissolving the sample, 2-3 drops of mixed indicator are added to the flask and excess HCl is neutralized with a 25% solution of NH_4OH until the appearance of a light rose color. The last drops of ammonia are poured in carefully without permitting a precipitate of magnesium oxide hydrate to fall out of solution.

Then the solution is transferred to a 250 ml measuring flask, having carefully washed out the conical flask with distilled water. The measuring flask is brought up to the mark by adding water.

10 ml of the prepared solution are transferred by means of a pipette to a conical flask. 10 ml ammonia-buffer solution and 7-8 drops of YeT-00 chromogen-black indicator are added. Volume is brought up to 50-75 ml with distilled water, after which the solution is slowly titrated with a 0.1 n solution of trilon B while intensively stirring until the color changes from raspberry red to blue.

Calculation: % MgO - 1.01 VC where:

V - amount ml. 0.1 n trilon B.

C - correction coefficient of trilon B.

$$T,0T = \frac{I,66 \cdot 250 \cdot 0,00I2I6}{5 \cdot I0}$$

$\frac{250}{5 \cdot 10}$ - dilution

1.66 - conversion factor of Mg^{2+}_{tot} for MgO.

G. Determination of MgO in the Magnesite Milk (concentration up to 1%)

The determination of MgO in strongly diluted magnesite milk is based upon the following reaction

$$MgO + 2HCl \longrightarrow MgCl_2 + H_2O$$

Reagents:

1. hydrochloric acid, 0.1 n solution
2. mixed indicator
3. caustic soda, 0.1 n solution

Course of the Analysis

A 25 ml milk sample is transferred to a 250 ml measuring flask, brought up to the mark with distilled water, carefully stirred, and then a 10 ml sample of solution is taken for analysis with a pipette. The sample taken with the pipette is placed in a conical 250 ml flask and diluted with up to 100 ml water. Several drops of mixed indicator are added, after which an exactly measured amount of 0.1 n HCl is added to the analyzed sample from a burette. Excess acid must be such that with complete solution of the sediment the solution is violet. Excess acid is titrated off with 0.1 n *

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* Translator's note: Part of the foreign text is missing.

Calculation:

$$MgO = \frac{(a - b) \cdot N \cdot 20 \cdot 250 \cdot 1000}{25 \cdot 10 \cdot 1000}, \text{ g/l or}$$

$$MgO = (a-b) \cdot C \cdot 2 \text{ g/l where:}$$

a - amount ml. 0.1 n NaOH required for titration of the amount of 0.1 n acid taken for analysis.

b - amount ml 0.1 n HCl used for inverse titration

C - correction coefficient of 0.1 n NaOH

N - normality of alkali

20 - gram equivalent of MgO

H. Determination of Iron, Aluminum and Calcium in the Magnesite

Determination is made according to methods of determining iron, aluminum and calcium in crystals.

A weighed quantity of 0.2 g is taken in determining calcium.

I. Analysis of the Magnesite Milk, Preparing It in a Mother Solution of Magnesium Sulfite-Sulfate

In preparing the magnesite milk in a mother solution, its analysis can be carried out just as when determining $MgSO_3$ and MgO in crystals.

The magnesium sulfite contained in the mother solution is oxidized by an iodine solution to magnesium sulfate:

$$MgSO_3 + I_2 + H_2O \longrightarrow MgSO_4 + 2HI$$

In this case, MgO can be bound to HCl

$$MgO + 2HCl \rightarrow MgCl_2 + H_2O$$

Reagents:

1. iodine, 0.1 n solution
2. hydrochloric acid 1 n solution HCl and diluted (1:1)
3. caustic soda, 1 n solution
4. mixed indicator
5. starch, 0.5% solution

Course of the Analysis

1 or 2 ml magnesite milk taken from a well-stirred sample are placed in a conical 500 ml flask into which 25 ml 0.1 n iodine solution and 25 ml 1 n HCl solution have been previously poured.

The contents of the flask are stirred and titrated with a 0.2 n solution of thiosulfate in the presence of starch. For best solution of MgO in the HCl, the titrated sample is heated for 10-20 minutes at a temperature of 70 - 80° C. After cooling the sample, 2-3 drops of mixed indicator are added and excess acid is titrated off with a 1 n solution of NaOH until the color changes from violet to green.

Calculation:

$$MgSO_3 = \frac{|a - a_1| \cdot C \cdot N \cdot 104,32 \cdot 1000}{V \cdot 2 \cdot 1000} \text{ g/l or}$$

$$= \frac{|a-a_1| \cdot C \cdot 5,2}{V} \text{ g/l, where}$$

a - amount ml. 0.1 n solution required to bind the quantity of 0.1 n iodine taken:

a_1 - amount ml. 0.1 n $Na_2S_2O_3$ solution spent on inverse titration of the unreacted iodine

N - normality of $Na_2S_2O_3$

C - correction coefficient of 0.1 n $Na_2S_2O_3$

V - amount ml. magnesite milk taken for analysis

The amount of MgO in the milk is calculated according to the following formula:

$$MgO = \frac{[b \cdot C_1 N_1 + (a - a_1) C N - S C N] 40.32 \cdot 1000}{V \cdot 2 \cdot 1000} \text{ g/l, where}$$

b - number ml 1 n NaOH solution required for titrating 25 ml 1 n HCl taken to dissolve MgO.

N_1 - normality of alkali

S - amount ml. 1 n NaOH spent on titrating the excess acid.

Note: The content of total magnesium is determined in the solution after determining $MgSO_3$, MgO and Mg^{2+}_{tot} is also found, as during the analysis of the sulfite-bisulfite solutions, i.e.,

$$Mg^{2+}_{tot} = \frac{OC \cdot 1.216}{V} \text{ g/l,}$$

after which one can approximately calculate the sulfate content:

$$MgSO_4 = [Mg^{2+}_{tot} - (0,231\, MgSO_3 + 0,6\, MgO)] \text{ g/l}$$

In this formula, the content of magnesium thiosulfate is not taken into account.

J. Determining MgO in the Magnesite Milk Prepared in Water by Density (concentration higher than 1%)

A 0.5 l (exactly 1) is taken as a sample from the magnesium milk and placed in a previously weighed graduated cylinder. When taking the sample, one ensures that the sample is characteristic for the concentration of milk existing in the device, and therefore each time the milk is poured into the cylinder or removed, it must be done with continuous stirring of the suspension.

The weight of the sample that has been taken is found according to the difference in weights of the cylinder with the sample, and empty, and

the density of the magnesium milk is found.

$$d = \frac{P}{V} \qquad g/cm^3$$

The contents of the milk are found according to density given in the table (for II-III-class magnesites)

TABLE

%	Density	%	Density
5	I.,039	I3	I,I08
6	I,048	I4	I,II7
7	I,056	I5	I,I26
8	I,065	I6	I,I35
9	I,074	I7	I,I43
I0	I,083	I8	I,I52
II	I,09I	I9	I,I6I
I2	I,I00	20	I,I70

12. Analysis of the Sediment

A. Preparing the Sample for Analysis

A sediment sample is dried at a temperature of 60-70° C, after which it is pulverized in a porcelain mortar and poured into a flask with the ground sample. The following are noted on the flask: designation of sample, place of sampling, date, time and sample number.

B. Determining Moistness

The determination of hygroscopic, crystallization and total moisture is made just as in the case of crystals of magnesium sulfite.

C. Determining $MgSO_3$, $MgSO_4$, MgO and Mg^{2+}_{tot} is Carried Out Just as in the Case of the Crystals

D. Determining Fe_2O_3, M_2O_3 and CaO

Determination is made the same as in the case of the crystals, and for determining CaO a weighed quantity of 0.2 g is taken.

E. Determining Organic Substances in the Sediment

The determination of organic substances (lubricating oils, etc.) is made from a measured quantity of sediment of 2 g, which is trapped on a filter in a funnel (previously dried and weighed) and washed with acetone (5-6 times). The filter with the washed sediment is placed in a drying cabinet and is dried at a temperature of t = 60-80° C, up to a constant weight.

Calculation: $\%\ (org.) = \frac{A-B}{A} \cdot 100$ where A - weight of weighed quantity taken (dry), g.

B - weight of weighed quantity, washed and dried, g.

F. Determination of the Residue Insoluble in Acid

2 g sediment powder are dissolved in a beaker (300-400 ml) in 120 ml HCl (1:1) during heating for a period of 20-25 minutes. After dissolving the weighed quantity, 100 ml distilled water are added to the sample and are filtered into a clean chemical beaker (for subsequent determination of magnesium sulfate in the weighed quantity) through a dried (at a temperature of t = 105° C) and weighed filter.

The sediment on the filter is washed with hot distilled water and is transferred to a drying cabinet, where the filter with the sediment is dried to a constant weight at a temperature no greater than 100 - 105° C.

Calculation:

$$\% \text{ I/R} = \frac{A - B}{g} .100, \quad \text{where}$$

A - weight of dry filter with residue, g

B - weight of dry filter, g

g - weighed quantity, g

Note: From the I/R (in acid), the following elements are determined - carbon, sulfur, SiO_2 and calcium.

13. Preparing the Reagents

A. Iodine Solutions

In order to prepare a 1 n solution of iodine, 127 g metallic iodine and 250 g KI are dissolved in 150 ml distilled water, carefully stirred, and then brought up to a solution volume of 1 liter. Solutions of 0.1 n and 0.02 n are prepared from 1 n solution by appropriate solution with distilled water.

B. Thiosulfate Solutions

In order to prepare a 1 n solution of thiosulfate, 248 g $Na_2S_2O_3$ are dissolved in 400-500 ml distilled water and are brought to a volume of 1 liter. 0.1 n and 0.02 n solutions are prepared from 1 n solution by appropriate dilution with distilled water.

a) Coefficient "C" of the 0.1 n solution of sodium thiosulfate is set according to the fixanal (fiksanal) of a 0.1 n potassium dichromate - $K_2Cr_2O_4$.

Course of the Determination

20 ml 10% KU (sic) and 20 ml (1:4) are placed in a conical flask. If the solution turns yellow in 1-2 minutes, the liberated iodine should bond with the thiosulfate while adding it drop by drop until total colorlessness is achieved. Then, 20 ml 0.1 n $K_2Cr_2O_7$ solution (fixanal/fiksanal) are added to the colorless solution from a pipette. The flask with its contents stands for 5 minutes in a dark spot for total liberation of iodine. Then the solution is diluted with up to 100 - 150 ml of distilled water and the liberated iodine is titrated out with a 0.1 n solution of sodium thiosulfate.

Calculation:

$$C_{Na_2S_2O_3} = \frac{V_{K_2Cr_2O_7} \cdot C_{K_2Cr_2O_7}}{V_{Na_2S_2O_3}}$$

Note: The coefficient of the 0.02 n solution of thiosulfate is established in the same fashion as for the 0.1 n solution of thiosulfate, but only by means of the 0.02 n solution of $K_2Cr_2O_7$ (fixanal). The fixanal solution of 0.02 n $K_2Cr_2O_7$ is prepared from a 0.1 n solution by appropriate solution with distilled water.

C. NaOH Solutions

For preparing 1 n NaOH solution, a 40 g weighed quantity of alkali is dissolved in 200 ml distilled water as the solution is brought up to 1 liter. 0.1 n solution is prepared by diluting 1 n solution.

a) Setting coefficient "C" of the 0.1 n solution of NaOH is carried out according to the fixanal of a 0.1 n solution of hydrochloric acid.

Course of the Determination

20 ml freshly prepared solution of 0.1 n HCl (fixanal) is taken up

by a pipette and transferred to a conical flask. 2-3 drops of mixed indicator are added, after which the solution is titrated with alkali until the color changes from violet to green.

Calculation:

$$C_{NaOH} = \frac{V_{HCl} \, C_{HCl}}{V_{NaOH}}$$

D. Solutions of Trilon "B" 0.1 n.

18.6 g trilon "B" are dissolved in 500 ml distilled water. The solution is filtered and transferred to a 1 liter measuring flask. The solution is brought up to 1 liter with water.

a) Setting coefficient "C" of 0.1 n trilon "B" is carried out by the fixanal of a 0.1 n solution of $MgSO_4$.

Course of the Determination

20 ml fixanal 0.1 n $MgSO_4$ are placed in a conical flask with a pipette. 100 ml water are poured into it and 10 ml ammonia buffer solution, 7-8 drops of YeT-00 chromogen-black indicator are added and the solution is slowly titrated with a 0.1 n solution of trilon "B" while energetically stirring. Titration is carried out until the color of the solution changes from raspberry to blue.

Calculation:

$$C_{Tr} = \frac{V_{Mg\,SO_4} \; C_{Mg\,SO_4}}{V_{Tr}}$$

E. The Ammonia Buffer Solution

For preparing the ammonia buffer solution, 100 ml 20% NH_4Cl solution and 100 ml 20% ammonia solution are mixed, after which the volume of the solution is brought up to 1 liter with water.

F. The Ammonium-Ammonia Buffer Solution

(Serves for separate determination of calcium and magnesium) 67.5 g NH_4Cl are dissolved in distilled water, 580 ml 25% ammonia solution are added and the solution is diluted with water to 1 liter.

G. Mixed Indicator

For preparing 100 ml indicator, a weighed quantity is taken: 0.1 g methylene blue and 0.2 g methylene red. The weighed quantities are individually dissolved in ethyl alcohol. The solutions are poured together and brought up to a volume of 100 ml. The indicator is stored in a dark place.

H. YeT-00 Chromogen-Black Indicator

0.5 g YeT-00 chromogen-black is dissolved in 10 ml ammonia buffer solution and the volume of the solution is brought up to 100 ml with ethyl alcohol.

PROBLEM 9a. A STUDY OF THE EFFECTIVENESS OF THE VENTURI ABSORBER DURING WORK ON HIGH TEMPERATURE GASES

As is known, in the magnesite method, depending upon the heat content of the gas being purified, tri- or hexasulfite crystals of magnesium form which possess varying degrees of solubility. Since it is namely the dissolved magnesium sulfite which is a chemically active component of the absorbent, it was of interest to assess the sorption capacity of the suspension based on the trisulfite crystals. A 2-stage apparatus with Venturi tubes and irrigation nozzles was chosen as an absorber.

The experiments were carried out on the experimental-operational device of the Northern Donetsk Thermoelectric Generating Station, which burns sulfur coal. The trisulfite crystals, as a rule, form during purification of the smokestack gases of the thermoelectric generating station, operating on masut* which is explained by the higher thermal content of the gases and the correspondingly higher temperature of the circulating suspension (above 50° C). In order to simulate the smokestack gases obtained from burning the masut, steam was dosed out into the gases of the Northern Donetsk Thermoelectric Generating Station, which made it possible to raise the temperature of the circulating absorption suspension from 48° C to 58-60° C. The indicated temperature regime facilitated the formation of magnesium trisulfite crystals.

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* Translator's note: Black petroleum oil.

Investigation of Hydraulic Resistance of the Venturi Absorber

The Venturi absorber consists of 2 sequentially mounted horizontal Venturi tubes with cross-sectional vents and an elbow-type drop catcher.

The hydraulic investigations were conducted in 2 stages. First, pressure drops during the passage of air through the apparatus without supplying irrigation were determined, after which they were determined during irrigation of the absorber with water. Water was supplied into the vent first along the path of the gas of the Venturi tube in the amount of $20 m^3/hr$, and into the second vent - $5 m^3/hr$.

Figure 1 shows the relationship of the coefficient of hydraulic resistance of the Venturi absorber calculated relative to the cross section of the first vent along the gas run without bringing up irrigation ζ dry, depending upon the Re criterion

$$Re_i = \frac{W_g^2 \cdot d_e}{\nu_g}$$

where W_g - velocity of air in the section of the first vent, m/sec,

d_e - equivalent diameter of first vent, m;

V_g -coefficient of kinematic viscosity of air, m^2/sec.

As can be seen from Figure 1, coefficient ζ will become practically constant, beginning with values of $Re_i \approx 10^6$, which corresponds to a gas velocity in the section of the first vent of $\approx$ 45 m/sec. The results of the hydraulic trials of the irrigated Venturi absorber are given in Table 1.

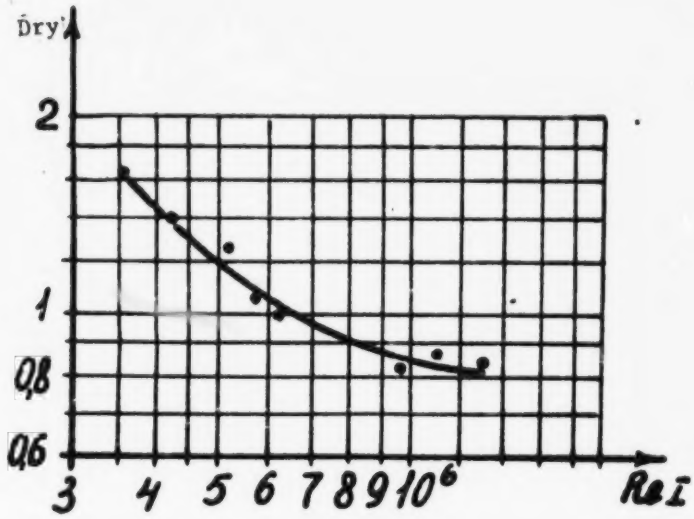

Figure 1. Relationship of hydraulic resistance of the absorber and Re.

TABLE 1.

RESULTS OF HYDRAULIC TRIALS OF THE IRRIGATED VENTURI ABSORBER

Volumetric flow rate of air, m^3/hr	Specific irrigation, l/m^3	Hydraulic resistance ΔP_1 kg/m^2	Hydraulic resistance ΔP_2 kg/m^2	Hydraulic resistance ΔP_{tot} kg/m^2	Note
I0000	2,50	24	8	45	
I2000	2,08	30	I6	52	
I4000	I,79	40	20	60	
I5600	I,60	46	24	70	
I7000	I,47	50	28	75	
I9200	I,30	60	38	I00	
2I900	I,I4	70	50	I70	
3I000	0,93	80	70	I70	
34800 →	0,80	I20	75	200	
	0,72	I30	80	2I0	

Investigation of the Content of Solid Particles in Gases

An analysis of the solid particles was made both before the absorber and after it, using the method of internal filtration.

At the intake to the absorber, the solid particles were basically ash which had not been trapped in the electrofilter. According to the obtained data, the content of ash particles in the gas comprises an average of 0.15 - 0.30 g/nm^3. At the output from the absorber, the solid particles in the gas consisted of ash and crystals formed in the apparatus and carried along with the spray. Since the spray discharge is proportional to the velocity of gas in the apparatus, the content of solid particles at the output from the apparatus increases with the increase in gas flow rate.

The content of solid particles after the absorber exceeds their content prior to the absorber by several times, which is the cause of the spray discharge.

A Study of Mass Exchange Characteristics of the Absorber

The task of this investigation was to determine the effectiveness of extracting sulfur dioxide from smokestack gases of the thermoelectric generating station with a change in the primary hydraulic parameters by the magnesite method in the turbulent Venturi scrubber.

The apparatus is a straight cross section vessel. Within the vessel, a 2-stage direct atomizer tube irrigated with nozzles is mounted horizontally. The irrigating liquid proceeds into the apparatus via 12 nozzles arranged in the following fashion (Figure 2): 6 nozzles (I, II groups) having a total productivity of 46 m^3/hr, are mounted at the intake point of first stage gas, 3 on each side; 4 nozzles (III group) with a total productivity of 28 m^3/hr are mounted above in the zone of the first stage diffuser, and 2 nozzles (IV group) with a total productivity of 5.4 m^3/hr are mounted on the second stage of the atomizer tube.

Types of mounted nozzles:

I and II groups - flat nozzle, impact, III group - spiral, IV - flat nozzle.

At the output of gas from the apparatus, a spray catching device of the elbow type is mounted with shaped walls and pockets. The experiments were carried out with the following technical parameters:

- concentration of SO_2 in gas in the apparatus - 0.09 - 0.15 tot.
- gas temperature - 80° C,
- concentration of O_2 in the gas - 3-5% tot.
- concentration of CO_2 in the gas, 8% tot.
- concentration of water vapor, 20% tot.
- ash content in gas - no more than 1 g/m^3,
- pH value of absorber solution at intake to apparatus - 7.5 - 6.0
- concentration of magnesium sulfite - 100 g /1
- concentration of magnesium sulfate - 150 - 200 g/1
- temperature of suspension - 58 - 60° C
- velocity of gas in vent of the first stage of absorption - 17.0 - 62.0 m/sec,
- irrigation - 8-80 m^3/hr.

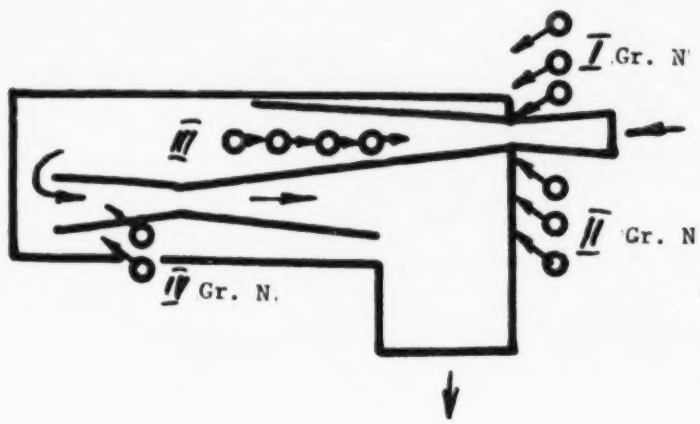

Figure 2. Diagram of arrangement of the nozzles.

Analyses of SO_2 in the gas were conducted using the iodometric method at the intake and output from the apparatus. The analysis of the suspension was carried out according to methods developed by NIIOGAZ and presented above.

The experiments were carried out with a constant flow rate of the gas and with a change in the amount of supplied liquid.

Processing of the experimental data was carried out via the degree of purification of the gas and the general coefficient of mass transfer relative to the surface area of the liquid mirror, which is approximately equal to the area of the horizontal cross section of the apparatus.

Motive force of the absorption process was accepted to be the mean arithmetical difference in the concentration of SO_2 in the gas at the beginning and end of the process.

In all of the experiments that were conducted, the height of the vent aperture of the first stage remained constant.

Figure 3 shows the relationship of the degree of gas purification and the density of irrigation and the velocity of the gas. As one can see from the graph, the degree of purification does not depend upon the velocity of the gas but only depends upon the amount of supplied suspension.

The plotted curve in Figure 2 is described by the following equation:

$$\eta = (0{,}006\,Q + 0{,}5) \cdot 100\ \% \qquad (2)$$

where Q - flow rate of liquid, $m^3/$ hr.

The experimental data were also processed through the coefficient of mass exchange. The cited graph relationships (Figure 4) are described by the following empirical formula:

$$C_g = 0{,}075\,W_g^{1,5}\left(\frac{4}{G}\right)^{0,5} \qquad (3)$$

here making changes as shown where Cg - coefficient of mass exchange relative to the cross section of the apparatus,

$$\frac{kg}{M^2/hr \quad mm.\ Hg}$$

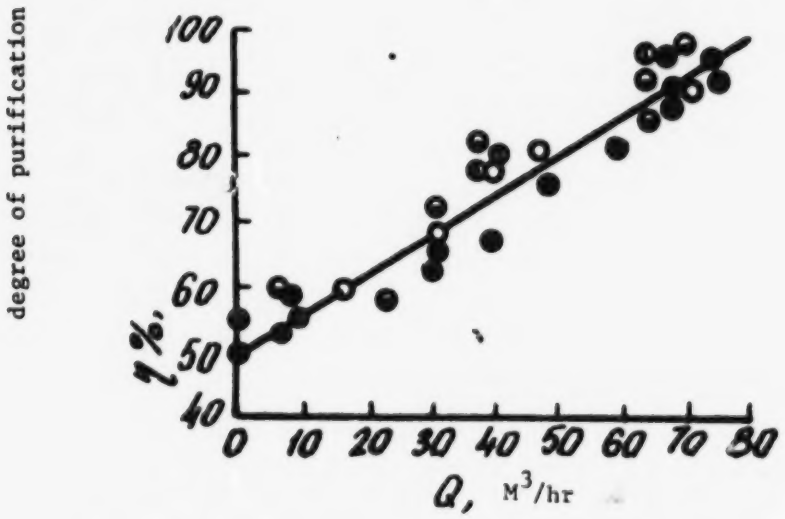

Figure 3. Relationship of the degree of purification of the gas and the density of irrigation and velocity of the g...

● - W_g = 17.8 m/sec
● - W_g = 30.0 m/sec
○ - W_g = 41.0 m/sec
● - W_g = 62.0 m/sec

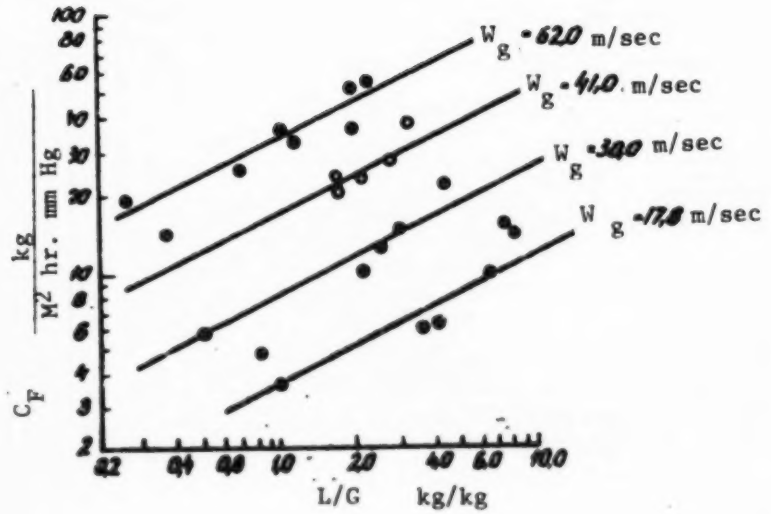

Figure 4. Relationship of the coefficient of mass exchange and the velocity of the gas and density of irrigation.

W_g - velocity of gas in vent, m/sec

L/G - ratio of the weight of the liquid to the weight of the gas, kg/kg.

A comparison was made of the effectiveness of operation of nozzles of the I and II groups with those of the III group (Figure 2) in the experiments. In operation of the I and II groups of nozzles, the degree of purification was approximately the same as during operation of the III group of nozzles. Consequently, purification of the gas of SO_2 does not depend upon the arrangement of nozzles in the turbulent absorber.

The results obtained in this study can be used for a comparative technical-economic design of a number of the studied high speed absorbers, with the goal of giving recommendations for employing the most promising of these in the practice of sulfur purification.